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(54) **Lead-free solder alloy**

(57) A lead-free solder alloy suitable for use in flow soldering of electronic components to printed wiring boards comprises 0.1 - 3 wt% of Cu, 0.001 - 0.1 wt% of P, optionally 0.001 - 0.1 wt% of Ge, and a balance of Sn. The solder alloy may further contain at least one element of Ag and Sb in a total amount of at most 4 wt%,

and/or at least one element of Ni, Co, Fe, Mn, Cr, and Mo in a total amount of at most 0.5 wt% in order to strengthen the alloy, and/or at least one element of Bi, In, and Zn in a total amount of at most 5 wt% in order to lower the melting point of the alloy.

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## Description

Background of the Invention

## 5 1. Field of the Invention

[0001] This invention relates to a lead-free solder alloy, and particularly to a lead-free solder alloy having excellent solderability when used for soldering electronic components to printed wiring boards by flow soldering.

## 10 2. Description of the Related Art

[0002] Printed circuit boards are used in a wide range of electrical and electronic equipment including home electrical appliances such as televisions, videos, refrigerators, and air conditioners, as well as office or home electronic equipment such as personal computers, printers, and copying machines. Typically a printed circuit board includes a number of electronic components such as LSI's, IC's, transistors, registers, and capacitors secured to a printed wiring board by soldering.

[0003] The solder to be employed for this purpose is selected taking into consideration the various properties and cost of the solder. Solder wettability or solderability on the surfaces of electronic components and printed wiring boards is one of the most important properties of a solder. If soldering is performed with solder having poor wettability, the resulting soldered joints may include soldering defects such as non-wetting, bridges, and voids.

[0004] Sn-Pb solders have long been used for soldering electronic components to printed wiring boards due to their low soldering temperatures, good solderability or solder wettability, and low cost. In particular, a 63% Sn-Pb solder, which is called a Sn-Pb eutectic solder or simply a eutectic solder due to its alloy composition near the eutectic composition for Sn-Pb alloys (61.9% Sn-Pb), is used in a wide variety of soldering applications, since it has a narrow solidification temperature range (which is the difference between the liquidus and solidus temperatures of the alloy) and can form reliable soldered joints. (In this specification, unless otherwise specified, the percent of an element in an alloy composition refers to mass percent or "wt%".)

[0005] When electrical or electronic equipment is discarded, it is usually disassembled to recover plastic parts such as housings and metallic parts such as chassis for recycling. However, printed circuit boards in the discarded equipment are not suitable for recycling, since they contain both metallic portions and plastic portions combined in a complicated manner. Therefore, in many cases, printed circuit boards removed from disassembled equipment are shredded and buried underground as industrial waste of a stabilized type.

[0006] In recent years, however, underground burial of lead-containing wastes including printed circuit boards has become an environmental problem. When the buried lead-containing wastes come into contact with acid rain (rain having a high acidity due to dissolving oxides of sulfur and nitrogen present in the atmosphere), the acid rain can dissolve lead from the wastes, and the dissolved lead can contaminate underground water. There is the concern that such contaminated water may cause lead poisoning if it is drunk by humans for long periods. To eliminate such environmental concerns, there is now a demand in the electronics industries for lead-free solders.

[0007] Lead-free solders which have been developed to date are based on Sn and contain one or more additional elements such as Cu, Ag, Bi, and Zn. Typical alloy compositions of lead-free solders are binary alloys such as Sn-0.7% Cu, Sn-3.5% Ag, Sn-58% Bi, and Sn-9% Zn, each having a composition which is the same as or close to the eutectic composition for the binary alloy system. Depending upon the use, additional alloying elements may be added to obtain a ternary or higher alloy.

[0008] Each of the above-mentioned lead-free solders has its own problems. For example, a Sn-Zn solder such as a Sn-9% Zn solder has the problem that Zn is highly susceptible to oxidation, resulting in the formation of a thick oxide film on the solder. As a result, wettability becomes poor if soldering is carried out in the air. In addition, when used in flow soldering, a Sn-Zn solder causes the formation of a large amount of dross, which causes difficult problems with respect to practical application of the solder.

[0009] With a Sn-Bi solder such as a Sn-58% Bi solder, the formation of dross during flow soldering is not a large problem, but due to the presence of a large proportion of Bi, which has poor ductility, the solder is brittle and has poor mechanical strength. Therefore, soldered joints formed from this solder may not be sufficiently reliable. There is a tendency for the mechanical strength of a Sn-Bi solder to decrease as the proportion of Bi increases.

[0010] At present, the lead-free solders which are considered most practical are Sn-Cu solders such as Sn-0.7% Cu, Sn-Ag solders such as Sn-3.5% Ag, and Sn-Ag-Cu solders (e.g., Sn-3.5% Sn-0.6% Cu) in which a small amount of Cu is added to a Sn-Ag solder.

[0011] Sn-Cu solders such as Sn-0.7% Cu are inexpensive and their unit cost is comparable to that of conventional Sn-Pb solders. However, they have poor solder wettability.

[0012] On the other hand, Sn-Ag solders such as Sn-3.5% Ag and Sn-Ag-Cu solders such as Sn-3.5% Ag-0.6% Cu

have relatively good solder wettability, and their mechanical strength is comparable or even superior to that of Sn-Pb solders. Thus, these solders are advantageous in their properties as a solder, but their cost is much higher than that of conventional Sn-Pb solders due to the presence of Ag, which is an expensive metal. If the Ag content in these solders is decreased in order to reduce costs, the wettability and the strength of the solders worsen.

**[0013]** Thus, there is a need for an improved lead-free solder which has the cost advantages of a Sn-Cu solder but has improved properties, and particularly improved wettability.

#### Summary of the Invention

**[0014]** The present inventors found that the addition of P (phosphorus) to a Sn-Cu lead-free solder alloy improves the wettability of the solder. Although this effect is obtained when P is added alone, the wettability of the solder can be further improved by the addition of P in combination with Ge (germanium).

**[0015]** According to one form of the present invention, a lead-free solder alloy comprises 0.1% - 3% of Cu, 0.001% - 0.1% of P, and a balance of Sn. According to another form of the present invention, a lead-free solder alloy comprises 0.1% - 3% of Cu, 0.001% - 0.1% of P, 0.001% - 0.1% of Ge, and a balance of Sn.

**[0016]** The lead-free solder alloy may further contain one or more additional elements which improve the mechanical strength or lower the melting point of the solder in an amount which does not have a significant adverse effect on other properties of the solder.

#### Detailed Description of the Invention

**[0017]** A Sn-based, lead-free solder alloy according to the present invention comprises 0.1% - 3% of Cu, 0.001% - 0.1% of P, and optionally 0.001% - 0.1% of Ge.

**[0018]** The presence of Cu in the solder alloy increases the mechanical strength of the solder. If the Cu content is smaller than 0.1%, Cu has no substantial effect in this respect. If the Cu content is larger than 3%, Cu increases the melting temperature of the solder significantly and reduces solder wettability. Furthermore, when melted to prepare a molten solder bath for use in flow soldering, such a Sn-Cu solder alloy containing more than 3% of Cu causes the formation of a large amount of dross, which makes the soldering operation cumbersome or difficult. Preferably, the Cu content is 0.3% - 1.5% and more preferably 0.4% - 1.0%.

**[0019]** The addition of P improves the wettability of a Sn-Cu solder. The wettability of the solder can be further improved by the combined addition of P and Ge.

**[0020]** Although it is not desired to be bound by a particular mechanism, it is thought that in a molten state of a solder alloy according to the present invention, P or P and Ge present in the solder are diffused toward the surface of the molten solder and oxidized at the surface to form a thin oxide layer, which serves to shield the surface of the molten solder from direct contact with the atmosphere, thereby preventing the oxidation of the molten solder and improving its wettability. The oxides of P tends to sublime at the temperature of the molten solder (around 250°C), while the oxides of Ge tends to remain for an extended time on the surface of the molten solder.

**[0021]** The addition of P or Ge to an Sn-Cu solder in an amount of smaller than 0.001% has no substantial effect on the wettability of the solder.

**[0022]** If P is added in an amount of larger than 0.1%, it forms a molten solder having a viscosity at its surface which is increased to an extent that may interfere with soldering operations, particularly in flow soldering, and cause soldering defects such as bridges, which are short circuits between adjacent soldered joints. Preferably, the P content is 0.001% - 0.05% and more preferably 0.001% - 0.01%.

**[0023]** Likewise, if the Ge content is larger than 0.1%, soldering operations may be impeded by an increased viscosity of molten solder at its surface. In this case, due to the above-described tendency for Ge to remain for an extended time on the surface, addition of Ge in an amount of more than 0.1% may cause more severe soldering defects such as non-wetting. When added, Ge is preferably present in an amount of 0.001% - 0.05% and more preferably 0.002% - 0.03%.

**[0024]** In the present invention, the addition of P or the combined addition of P and Ge to a lead-free, Sn-Cu solder is effective in improving wettability, but it does not increase the mechanical strength of the solder alloy. The mechanical strength of a Sn-Cu solder alloy is generally inferior to that of a Sn-Ag or Sn-Ag-Cu solder alloy. Therefore, when it is desired to improve both wettability and mechanical strength, one or more strength-improving elements which are effective in improving the strength of a Sn-based solder alloy can be added to the Sn-Cu-P or Sn-Cu-P-Ge solder alloy according to the present invention.

**[0025]** Examples of such strength-improving elements are Ag, Sb, Ni, Co, Fe, Mn, Cr, and Mo. Each of these elements forms either a solid solution in Sn or an intermetallic compound with Sn in a Sn-Cu-based solder alloy, thereby improving the mechanical strength of the alloy. However, if the content of such elements is too large, they substantially elevate the liquidus temperature of the solder. As a result, the fluidity of molten solder at a given soldering temperature is

decreased. For this reason, the total content of Ag and Sb is at most 4%, preferably at most 3.5%, and more preferably at most 3%, and the total content of Ni, Co, Fe, Mn, Cr, and Mo is at most 0.5% and preferably at most 0.3%.

[0026] Sn-Cu solders, Sn-Ag solders, and Sn-Ag-Cu solder, which are considered to be promising as lead-free solders, have a melting point which is considerably higher than that of Sn-Pb solders. At present, most electronic components are designed for soldering with Sn-Pb solders. When such electronic components are mounted on a printed wiring board by soldering with one of the above-described higher-melting, lead-free solders, the electronic components may possibly be thermally damaged during soldering so that they cannot operate properly.

[0027] In order to eliminate or minimize such thermal damage of electronic components during soldering, a lead-free solder alloy according to the present invention may contain one or more elements for lowering the melting point of a Sn-based solder alloy. Examples of such melting point-lowering elements are Bi, In, and Zn. However, these elements have problems when added in a large amount. Specifically, Bi has poor ductility and can degrade the mechanical strength of a solder alloy, as described previously. Indium (In) and Zn are highly susceptible to oxidation to form oxides, which can interfere with soldering performed near the surface of molten solder such as wave soldering, as previously discussed with respect to P and Ge. Therefore, when added, the total content of Bi, In, and Zn in a lead-free solder alloy according to the present invention is at most 5% and preferably at most 3%.

[0028] A lead-free solder alloy according to the present invention can have a wide variety of shapes and forms, which include but are not limited to rods, wires, ribbons, pellets, discs, washers, balls, and other shapes, as well as powders. The powder form of the solder alloy may be used to prepare a solder paste.

[0029] Although a lead-free solder alloy according to the present invention may be used in various soldering methods, it is particularly suitable for use in flow soldering which includes wave soldering and dip soldering and which uses a molten solder bath. The lead-free solder alloy is more particularly suitable for use in wave soldering of electronic components to printed wiring boards. In wave soldering, a wave is formed in a molten solder bath by means of a pump and a nozzle, for example, and the surface to be soldered (e.g., the back surface of a printed wiring board on which electronic parts have been placed) is brought into contact with the wave while being traveled in a horizontal direction above the solder bath.

[0030] When a lead-free solder alloy according to the present invention is used to perform flow soldering and particularly wave soldering in a continuous process using a molten solder bath, the P content of the solder alloy in the bath may decrease with time due to sublimation of its oxides formed at the surface of the bath as described above. If necessary, the alloy composition may be adjusted during the continuous soldering operation by addition of one or more elements which are insufficient in the bath. The added elements may be in the form of an alloy with other alloying elements.

#### Examples

[0031] A number of Sn-Cu-based, lead-free solder alloys were prepared by casting and were subjected to tests for evaluating their wettability and bulk strength. The compositions of the solder alloys and the test results are shown in the following table, in which Examples 1 to 7 illustrate solder alloys according to the present invention.

	Composition (wt%)								Properties	
	Sn	Cu	P	Ge	Ag	Ni	Bi	Sb	Wettability	Bulk strength (MPa)
Example 1	Bal.	0.5	0.005						Excellent	32
Example 2	Bal.	0.7	0.01						Excellent	36
Example 3	Bal.	0.7	0.005	0.01					Excellent	36
Example 4	Bal.	0.5	0.005		0.3				Excellent	37
Example 5	Bal.	0.7	0.01					0.3	Good	36
Example 6	Bal.	0.7	0.003	0.01		0.05			Good	33
Example 7	Bal.	0.5	0.005		2		2		Excellent	73
Comparative Example 1	Bal.	0.7							Poor	31
Comparative Example 2	Bal.	0.7						0.3	Poor	31

[0032] The wettability of each solder alloy was tested by the wetting balance test (meniscograph method) using a standard testing apparatus for the test. The test pieces used as a substrate to be wetted by a molten solder were Cu plates which measured 0.3 mm thick x 10 mm wide x 30 mm long and which had been subjected to oxidizing treatment. In the test, after a soldering flux was applied to the surface of a test piece, the test piece was moved downward into a molten bath of the solder alloy to be tested which was maintained at 250°C and then pulled up from the molten bath while measuring the load placed on the test piece to obtain a curve of wetting force as a function of time. The wettability was evaluated by the zero crossing time on this curve in the following manner:

Excellent: zero crossing time of less than 2 seconds;  
 Good: zero crossing time of at least 2 seconds and less than 3 seconds;  
 Poor: zero crossing time of 3 seconds or longer.

[0033] The bulk strength of each solder alloy was measured using a test piece of the solder alloy having the shape specified as JIS Z 2201 No. 4 Test Piece. The test piece was prepared by machining a cast bar of the solder alloy. The test piece was subjected to a tensile test using a universal testing machine with a crosshead speed corresponding to approximately 20 %/min of the gauge length of the test piece. The maximum stress was recorded as the bulk strength.

[0034] As can be seen from the table, each solder alloy according to the present invention has good wettability in spite of being an inexpensive Sn-Cu-based solder, thereby making it possible to perform soldering operations with such a solder in a stable manner.

[0035] Although the present invention has been described with respect to preferred embodiments, they are mere illustrative and not intended to limit the present invention. It should be understood by those skilled in the art that various modifications and variations of the embodiments described above can be employed without departing from the scope of the present invention as set forth in the claims.

#### Claims

1. A lead-free solder alloy which consists essentially of 0.1 - 3 wt% of Cu, 0.001 - 0.1 wt% of P, optionally 0.001 - 0.1 wt% of Ge, optionally one or more strength-improving elements, optionally one or more melting point-lowering elements, and a balance of Sn.
2. A lead-free solder alloy as claimed in claim 1 wherein the one or more strength-improving elements comprise at least one of Ag and Sb in a total amount of at most 4 wt%.
3. A lead-free solder alloy as claimed in claim 1 wherein the one or more strength-improving elements comprise at least one element selected from the group consisting of Ni, Co, Fe, Mn, Cr, and Mo in a total amount of at most 0.5 wt%.
4. A lead-free solder alloy as claimed in any one of claims 1 to 3 wherein the one or more melting point-lowering elements comprise at least one of Bi, In, and Zn in a total amount of at most 5 wt%.
5. A soldered joint formed from a lead-free solder alloy as claimed in any one of claims 1 to 4.
6. A soldered joint as claimed in claim 5 wherein the soldered joint is formed by flow soldering.
7. A method of performing flow soldering comprising using a lead-free solder alloy as claimed in any one of claims 1 to 4.
8. A method as claimed in claim 7 wherein the flow soldering is wave soldering.



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# EUROPEAN SEARCH REPORT

Application Number  
EP 02 29 1590

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IntCl.7)
X	US 5 980 822 A (PARK CHUL-WOO ET AL) 9 November 1999 (1999-11-09) * claim *	1,2,4,5	B23K35/26
X	EP 0 336 575 A (COOKSON GROUP PLC) 11 October 1989 (1989-10-11) * example 2 *	1,2,4,5	
X	WO 01 03878 A (MULTICORE SOLDERS LTD STEEN HECTOR ANDREW HAMILTON (GB)) 18 January 2001 (2001-01-18) * claims *	1,2,4-8	
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 20, 10 July 2001 (2001-07-10) & JP 2001 071173 A (ISHIKAWA KINZOKU KK), 21 March 2001 (2001-03-21) * abstract *	1-3	
X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 04, 31 August 2000 (2000-08-31) & JP 2000 015476 A (ISHIKAWA KINZOKU KK), 18 January 2000 (2000-01-18) * abstract *	1-4	TECHNICAL FIELDS SEARCHED (IntCl.7) B23K
X	PATENT ABSTRACTS OF JAPAN vol. 1998, no. 06, 30 April 1998 (1998-04-30) & JP 10 034376 A (NIPPON GENMA:KK), 10 February 1998 (1998-02-10) * abstract *	1-4	
A	EP 1 106 301 A (NIPPON SHEET GLASS CO LTD) 13 June 2001 (2001-06-13) -/-		
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 9 October 2002	Examiner Mollet, G
<p>CATEGORY OF CITED DOCUMENTS</p> <p>X: particularly relevant if taken alone Y: particularly relevant if combined with another document of the same category A: technological background O: non-written disclosure P: intermediate document</p> <p>T: theory or principle underlying the invention E: earlier patent document, but published on, or after the filing date D: document cited in the application L: document cited for other reasons &amp;: member of the same patent family, corresponding document</p>			

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# EUROPEAN SEARCH REPORT

Application Number  
EP 02 29 1590

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.7)
A	EP 0 855 242 A (SENJU METAL INDUSTRY CO ; MATSUSHITA ELECTRIC IND CO LTD (JP)) 29 July 1998 (1998-07-29) -----		
			TECHNICAL FIELDS SEARCHED (Int.Cl.7)
The present search report has been drawn up for all claims			
Place of search <b>THE HAGUE</b>		Date of completion of the search <b>9 October 2002</b>	Examiner <b>Mollet, G</b>
<p><b>CATEGORY OF CITED DOCUMENTS</b></p> <p>X : particularly relevant if taken alone  Y : particularly relevant if combined with another document of the same category  A : technological background  O : non-written disclosure  P : intermediate document</p> <p>T : theory or principle underlying the invention  E : earlier patent document, but published on, or after the filing date  D : document cited in the application  L : document cited for other reasons</p> <p>&amp; : member of the same patent family, corresponding document</p>			

EPO FORM 1503 03 92 (P2-A1-1)

ANNEX TO THE EUROPEAN SEARCH REPORT  
ON EUROPEAN PATENT APPLICATION NO.

EP 02 29 1590

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

09-10-2002

Patent document cited in search report		Publication date		Patent family member(s)	Publication date
US 5980822	A	09-11-1999	CN	1195592 A	14-10-1998
			JF	2885773 B2	26-04-1999
			JF	10225790 A	25-08-1998
EP 0336575	A	11-10-1989	AU	3167289 A	05-10-1989
			CA	1299470 A1	28-04-1992
			EP	0336575 A1	11-10-1989
			JP	2070033 A	08-03-1990
			US	4929423 A	29-05-1990
			ZA	8902041 A	28-03-1990
WO 0103878	A	18-01-2001	AU	5556800 A	30-01-2001
			WO	0103878 A1	18-01-2001
			GB	2367834 A	17-04-2002
JP 2001071173	A	21-03-2001	NONE		
JP 2000015476	A	18-01-2000	NONE		
JP 10034376 6	A		NONE		
EP 1106301	A	13-06-2001	EP	1106301 A1	13-06-2001
			US	6319461 B1	20-11-2001
			CN	1313802 T	19-09-2001
			WO	0076717 A1	21-12-2000
			JF	2001058287 A	06-03-2001
EP 0855242	A	29-07-1998	JP	9094687 A	08-04-1997
			JP	3299091 B2	08-07-2002
			JP	9094688 A	08-04-1997
			JP	9253882 A	30-09-1997
			EP	0855242 A1	29-07-1998
			US	6241942 B1	05-06-2001
			CN	1198117 A, B	04-11-1998
			WO	9712719 A1	10-04-1997
			US	2002015660 A1	07-02-2002

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For more details about this annex: see Official Journal of the European Patent Office, No. 12/82